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(54) Title: A DETERGENT COMPOSITION (57) Abstract The present invention relates to detergent compositions comprising anionic mid-branched surfactant compounds and a bleaching system comprising a hydrophobic and a hydrophilic bleach precursor. The compositions are particularly useful as solid laundry detergent compositions.		

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A Detergent Composition

Technical Field

The present invention relates to detergent compositions comprising anionic mid-branched surfactant compounds and a bleaching system comprising a hydrophobic and a hydrophilic bleach precursor. The compositions are particularly useful as solid laundry detergent compositions.

Background to the Invention

Recently, a certain new type of anionic mid-chain branched surfactants has been developed. These surfactants are described in unpublished co-pending applications US 97/06485, US 97/06474, US 97/06339, US 97/06476 and US 97/06338.

It has been determined that these mid-chain branched surfactants are excellent surfactants, in particular for use in laundry products, especially under cool or cold water washing conditions even as low as 20°C-5°C. It has also been found that combination of two or more of these mid-chain branched surfactants can provide a surfactant mixture that is even higher in surfactancy and has better low temperature water solubility.

A component traditionally present in most detergents is a bleach. Various bleaching systems have been developed over the past decades, such as bleaching systems, based on organic peroxyacids. The organic peroxyacids are often obtained by the in situ perhydrolysis of organic peroxyacid bleach precursor compounds (bleach activators).

However, it is generally known that a variety of other detergent ingredients, commonly used in detergent, are not always (fully) bleach compatible, for example certain surfactants, perfumes, enzymes. These ingredient can react with the bleach, which results in a reduction of the performance of both the bleach and these

ingredients. It is thus desirable to formulate detergents which comprise as little bleach as necessary to obtain an excellent bleaching performance, and to formulate the detergents with bleach compatible ingredients

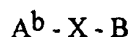
It has now been found these mid-chain branched surfactants are very bleach compatible. Furthermore, it has been found that detergent compositions comprising these mid-chain branched surfactants and a mixed bleaching system, comprising hydrophobic and hydrophilic bleach precursors, an excellent bleaching and cleaning performance is achieved, even when low amounts of bleach are used. It has surprisingly been found that both hydrophilic and hydrophobic, bleachable and non-bleachable stains and soils are more effectively removed. Without being bound by theory, it is believed that this is due to the excellent stain and soil removal by the mid-chain branched surfactant, which facilitates the access to the remaining bleachable stains and soils by the hydrophobic and hydrophilic bleaches and allows these bleaches to bleach very effectively these remaining bleachable stains. Another additional benefit is that by the reduction of the amount of bleach which is required for a good bleaching performance, the ease of formulation can be improved and the formulation costs can be reduced.

All documents cited are hereby incorporated herein by reference.

Summary of the invention

The invention relates to detergent compositions comprising

a) at least 0.5%, preferably at least 5%, more preferably at least 10% by weight of the composition a surfactant system, comprising one or more longer alkyl chain, mid-chain branched surfactant compounds of the formula:



wherein:

(1) A^b is a hydrophobic mid-chain branched alkyl moiety, having in total 9 to 22 carbons in the moiety, preferably from 12 to about 18, having: (1) a longest linear carbon chain attached to the - X - B moiety in the range of from 8 to 21 carbon atoms; (2) one or more $C_1 - C_3$ alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a

carbon of the longest linear carbon chain at a position within the range of the position 2 carbon, counting from position 1 carbon (#1) which is attached to the - X - B moiety, to the position of the terminal carbon minus 2 carbons, (the $(\omega - 2)$ carbon); and (4) when more than one of these compounds is present, the average total number of carbon atoms in the A^b-X moieties in the above formula is within the range of greater than 14.5 to about 18, preferably from about 15 to about 17;

(II) B is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, preferably polyoxyethylene and polyoxypropylene, alkoxyated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polygluconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccinates, polyalkoxyated carboxylates, glucamides, taurinates, sarcosinates, glycinate, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxyated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkylated/polyhydroxyalkylated quats, alkylated quats, alkylated/polyhydroxyalkylated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and

(III) X is selected from $-CH_2-$ and $-C(O)-$; and

b) at least 0.5% by weight of the composition a bleaching system comprising

(I) a hydrophobic bleach precursor; and

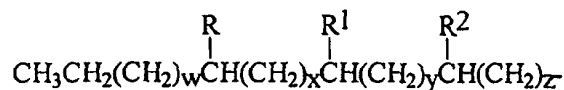
(II) a hydrophilic bleach precursor.

Detailed description of the invention

Mid-chain branched surfactant compounds-containing surfactant system

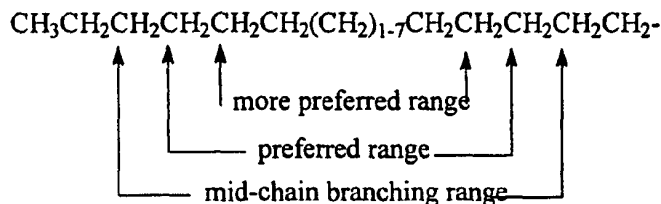
The detergent compositions of the invention comprise at least 0.5%, preferably at least 5%, more preferably at least 10% by weight of the composition of a surfactant system, comprising longer alkyl chain, mid-chain branched surfactant compounds, selected from the group consisting of surfactant compounds having the formula as defined above.

Preferred surfactant systems herein comprise longer alkyl chain, mid-chain branched surfactant compounds of the above formula wherein the A^b moiety is a branched primary alkyl moiety having the formula:



wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula (including the R, R^1 , and R^2 branching) is from 13 to 19; R, R^1 , and R^2 are each independently selected from hydrogen and C_1 - C_3 alkyl (preferably methyl), provided R, R^1 , and R^2 are not all hydrogen and, when z is 0, at least R or R^1 is not hydrogen; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer from 0 to 13; and $w + x + y + z$ is from 7 to 13.

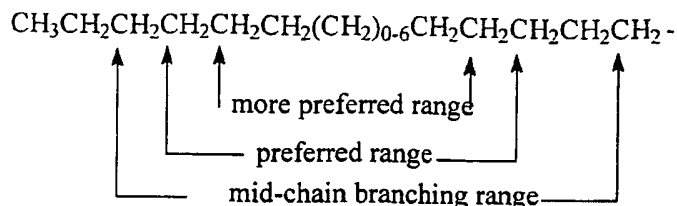
In general, for the mid-chain branched surfactant compounds of the surfactant system, certain points of branching (e.g., the location along the chain of the R, R^1 , and/or R^2 moieties in the above formula) are preferred over other points of branching along the backbone of the surfactant. The formula below illustrates the mid-chain branching range (i.e., where points of branching occur), preferred mid-chain branching range, and more preferred mid-chain branching range for mono-methyl branched alkyl A^b moieties useful according to the present invention.



It should be noted that for the mono-methyl substituted surfactants these ranges exclude the two terminal carbon atoms of the chain and the carbon atom immediately adjacent to the -X - B group.

The formula below illustrates the mid-chain branching range, preferred mid-chain branching range, and more preferred mid-chain branching range for di-methyl substituted alkyl A^b moieties useful according to the present invention.

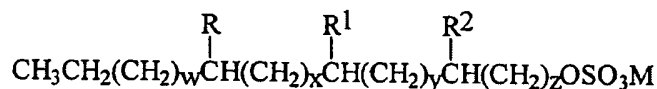
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Preferred are surfactant compounds wherein in the above formula the A^b moiety does not have any quaternary substituted carbon atoms (i.e., 4 carbon atoms directly attached to one carbon atom).

The most preferred mid-chain branched surfactants compounds for use in the detergent compositions herein are mid-chain branched primary alkyl sulfonate and, even more preferably, sulfate surfactants. It should be understood that for the purpose of the invention, it may be preferred that the surfactant system comprises a mixture of two or more mid-chain branched primary alkyl sulfate or sulphonate surfactants.

Preferred mid-chain branched primary alkyl sulfate surfactants are of the formula

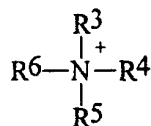


These surfactants have a linear primary alkyl sulfate chain backbone (i.e., the longest linear carbon chain which includes the sulfated carbon atom) which preferably comprises from 12 to 19 carbon atoms and their branched primary alkyl moieties comprise preferably a total of at least 14 and preferably no more than 20, carbon atoms. In the surfactant system comprising more than one of these sulfate surfactants, the average total number of carbon atoms for the branched primary alkyl moieties is preferably within the range of from greater than 14.5 to about 17.5.

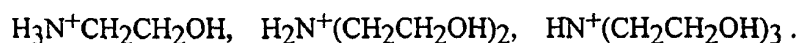
Thus, the surfactant system preferably comprises at least one branched primary alkyl sulfate surfactant compound having a longest linear carbon chain of not less than 12 carbon atoms or not more than 19 carbon atoms, and the total number of carbon atoms including branching must be at least 14, and further the average total number of carbon atoms for the branched primary alkyl moiety is within the range of greater than 14.5 to about 17.5.

R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl group (preferably hydrogen or C₁-C₂ alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R, R¹, and R² are not all hydrogen. Further, when z is 1, at least R or R¹ is not hydrogen.

M is hydrogen or a salt forming cation depending upon the method of synthesis. Examples of salt forming cations are lithium, sodium, potassium, calcium, magnesium, quaternary alkyl amines having the formula



wherein R³, R⁴, R⁵ and R⁶ are independently hydrogen, C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₆ alkanol, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, and mixtures thereof. Preferred cations are ammonium (R³, R⁴, R⁵ and R⁶ equal hydrogen), sodium, potassium, mono-, di-, and trialkanol ammonium, and mixtures thereof. The monoalkanol ammonium compounds of the present invention have R³ equal to C₁-C₆ alkanol, R⁴, R⁵ and R⁶ equal to hydrogen; dialkanol ammonium compounds of the present invention have R³ and R⁴ equal to C₁-C₆ alkanol, R⁵ and R⁶ equal to hydrogen; trialkanol ammonium compounds of the present invention have R³, R⁴ and R⁵ equal to C₁-C₆ alkanol, R⁶ equal to hydrogen. Preferred alkanol ammonium salts of the present invention are the mono-, di- and tri- quaternary ammonium compounds having the formulas:



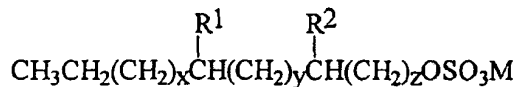
Preferred M is sodium, potassium and the C₂ alkanol ammonium salts listed above; most preferred is sodium.

Further regarding the above formula, w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer of at least 1; and w + x + y + z is an integer from 8 to 14.

A preferred mid-chain branched primary alkyl sulfate surfactant is, a C₁₆ total carbon primary alkyl sulfate surfactant having 13 carbon atoms in the backbone and having 1, 2, or 3 branching units (i.e., R, R¹ and/or R²) of in total 3 carbon atoms,

(whereby thus the total number of carbon atoms is at least 16). Preferred branching units can be one propyl branching unit or three methyl branching units.

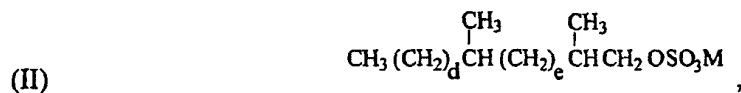
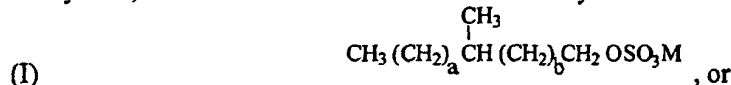
Another preferred surfactant system of the present invention have one or more branched primary alkyl sulfates having the formula



wherein the total number of carbon atoms, including branching, is from 15 to 18, and when more than one of these sulfates is present, the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than 14.5 to about 17.5; R^1 and R^2 are each independently hydrogen or C_1 - C_3 alkyl; M is a water soluble cation; x is from 0 to 11; y is from 0 to 11; z is at least 2; and $x + y + z$ is from 9 to 13; provided R^1 and R^2 are not both hydrogen.

Preferably, the surfactant system comprises at least 20% by weight of the system, more preferably at least 60% by weight, even more preferably at least 90% by weight of the system, of a mid chain branched primary alkyl sulfates, preferably having R^1 and R^2 independently hydrogen or methyl, provided R^1 and R^2 are not both hydrogen; $x + y$ is equal to 8, 9, or 10 and z is at least 2, whereby the average total number of carbon atoms in these sulfate surfactants is preferably from 15 to 17, more preferably from 16-17.

Furthermore, preferred surfactant systems are those, which comprise at least about 20%, more preferably at least 60%, even more preferably at least 90% by weight of the system, of one or more mid-chain branched alkyl sulfates having the formula:



or mixtures thereof; wherein M represents one or more cations; a, b, d, and e are integers, $a+b$ is from 10 to 16, $d+e$ is from 8 to 14 and wherein further when $a + b = 10$, a is an integer from 2 to 9 and b is an integer from 1 to 8; when $a + b = 11$, a is an integer from 2 to 10 and b is an integer from 1 to 9; when $a + b = 12$, a is an integer from 2 to 11 and b is an integer from 1 to 10;

when $a + b = 13$, a is an integer from 2 to 12 and b is an integer from 1 to 11;
when $a + b = 14$, a is an integer from 2 to 13 and b is an integer from 1 to 12;
when $a + b = 15$, a is an integer from 2 to 14 and b is an integer from 1 to 13;
when $a + b = 16$, a is an integer from 2 to 15 and b is an integer from 1 to 14;
when $d + e = 8$, d is an integer from 2 to 7 and e is an integer from 1 to 6;
when $d + e = 9$, d is an integer from 2 to 8 and e is an integer from 1 to 7;
when $d + e = 10$, d is an integer from 2 to 9 and e is an integer from 1 to 8;
when $d + e = 11$, d is an integer from 2 to 10 and e is an integer from 1 to 9;
when $d + e = 12$, d is an integer from 2 to 11 and e is an integer from 1 to 10;
when $d + e = 13$, d is an integer from 2 to 12 and e is an integer from 1 to 11;
when $d + e = 14$, d is an integer from 2 to 13 and e is an integer from 1 to 12;
whereby, when more than one of these sulfate surfactants is present in the surfactant system, the average total number of carbon atoms in the branched primary alkyl moieties having the above formulas is within the range of greater than 14.5 to about 17.5.

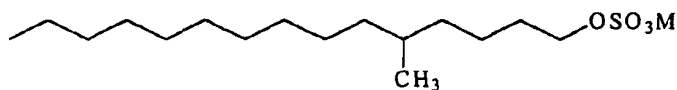
Preferred mono-methyl branched primary alkyl sulfates are selected from the group consisting of: 3-methyl pentadecanol sulfate, 4-methyl pentadecanol sulfate, 5-methyl pentadecanol sulfate, 6-methyl pentadecanol sulfate, 7-methyl pentadecanol sulfate, 8-methyl pentadecanol sulfate, 9-methyl pentadecanol sulfate, 10-methyl pentadecanol sulfate, 11-methyl pentadecanol sulfate, 12-methyl pentadecanol sulfate, 13-methyl pentadecanol sulfate, 3-methyl hexadecanol sulfate, 4-methyl hexadecanol sulfate, 5-methyl hexadecanol sulfate, 6-methyl hexadecanol sulfate, 7-methyl hexadecanol sulfate, 8-methyl hexadecanol sulfate, 9-methyl hexadecanol sulfate, 10-methyl hexadecanol sulfate, 11-methyl hexadecanol sulfate, 12-methyl hexadecanol sulfate, 13-methyl hexadecanol sulfate, 14-methyl hexadecanol sulfate, and mixtures thereof.

Preferred di-methyl branched primary alkyl sulfates are selected from the group consisting of: 2,3-methyl tetradecanol sulfate, 2,4-methyl tetradecanol sulfate, 2,5-methyl tetradecanol sulfate, 2,6-methyl tetradecanol sulfate, 2,7-methyl tetradecanol sulfate, 2,8-methyl tetradecanol sulfate, 2,9-methyl tetradecanol sulfate, 2,10-methyl tetradecanol sulfate, 2,11-methyl tetradecanol sulfate, 2,12-methyl tetradecanol sulfate, 2,3-methyl pentadecanol sulfate, 2,4-methyl pentadecanol sulfate, 2,5-methyl pentadecanol sulfate, 2,6-methyl pentadecanol sulfate, 2,7-methyl pentadecanol sulfate, 2,8-methyl pentadecanol sulfate, 2,9-methyl pentadecanol sulfate, 2,10-methyl pentadecanol sulfate, 2,11-methyl pentadecanol sulfate, 2,12-methyl pentadecanol sulfate, and mixtures thereof.

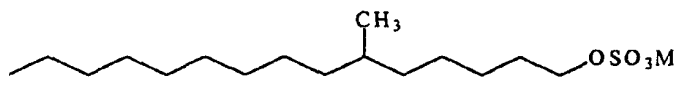
sulfate, 2,10-methyl pentadecanol sulfate, 2,11-methyl pentadecanol sulfate, 2,12-methyl pentadecanol sulfate, 2,13-methyl pentadecanol sulfate, and mixtures thereof.

The following branched primary alkyl sulfates comprising 16 carbon atoms and having one branching unit are examples of preferred branched surfactants useful in the present invention compositions:

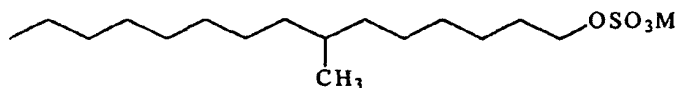
5-methylpentadecylsulfate having the formula:



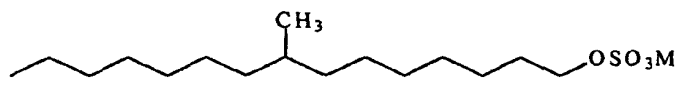
6-methylpentadecylsulfate having the formula



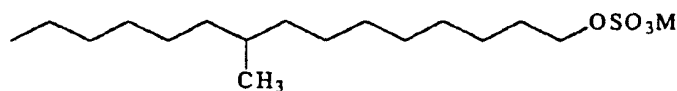
7-methylpentadecylsulfate having the formula



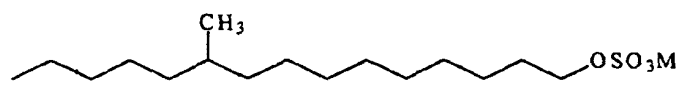
8-methylpentadecylsulfate having the formula



9-methylpentadecylsulfate having the formula



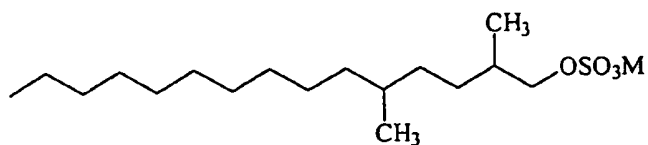
10-methylpentadecylsulfate having the formula



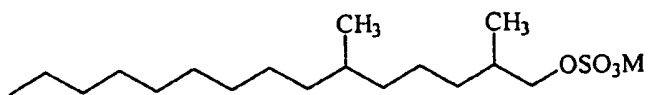
wherein M is preferably sodium.

The following branched primary alkyl sulfates comprising 17 carbon atoms and having two branching units are examples of preferred branched surfactants according to the present invention:

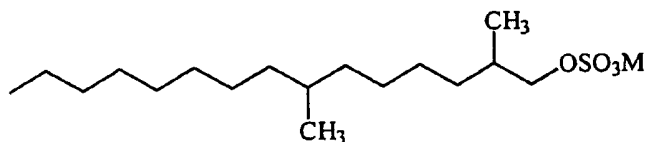
2,5-dimethylpentadecylsulfate having the formula:



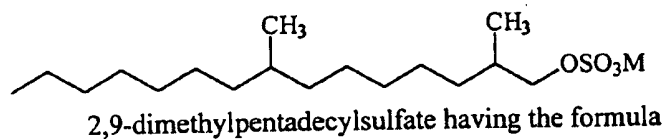
2,6-dimethylpentadecylsulfate having the formula



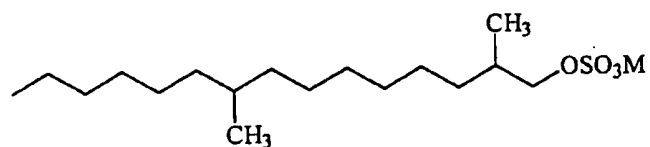
2,7-dimethylpentadecylsulfate having the formula



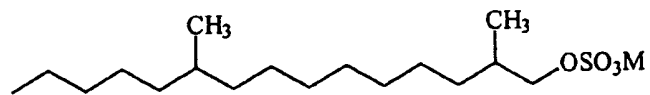
2,8-dimethylpentadecylsulfate having the formula



2,9-dimethylpentadecylsulfate having the formula



2,10-dimethylpentadecylsulfate having the formula



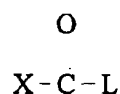
wherein M is preferably sodium.

Bleaching system

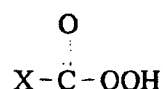
The bleaching system of the invention comprises a hydrophobic and a hydrophilic bleach precursor.

The bleaching system is present at a level of at least 0.5% by weight of the composition, preferably from 0.5% to 45% by weight, more preferably from 1% to 30% by weight, most preferably from 1.5% to 25% by weight of the detergent compositions.

Preferably, the bleach precursors are peroxyacid bleach precursors which may be represented as



where L is a leaving group and X is essentially any functionality, which determines for the present invention whether the precursor is hydrophobic or hydrophilic, and which is such that on perhydrolysis the structure of the peroxyacid produced is



The hydrophobic bleach of the present invention comprises a group X which contain at least 6 carbon atoms. The hydrophilic bleach of the present invention comprises a group X which contain less than 6 carbon atoms.

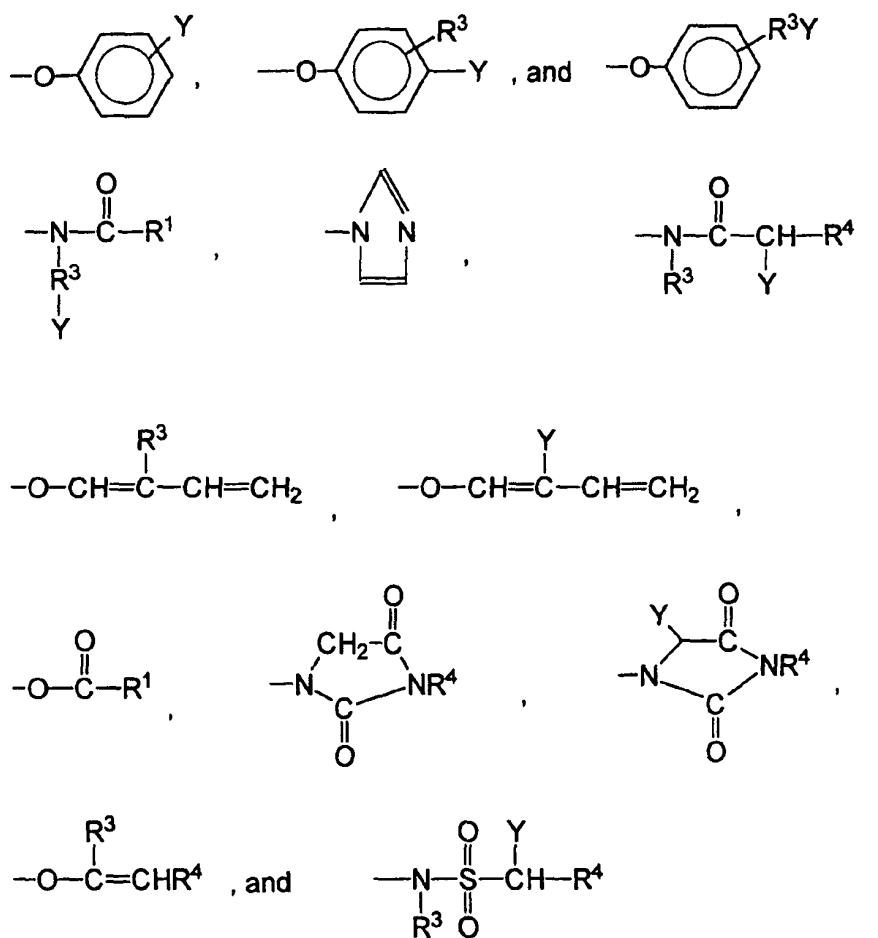
Preferably, the bleaching system of the invention contains a hydrogen peroxide source and a hydrophilic and hydrophobic (organic peroxyacid) bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursors with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. Preferred perhydrate bleaches are metal perborates, metal percarbonates, particularly the sodium salts. Perborate can be mono or tetra hydrated. Sodium percarbonate has the formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. Potassium or sodium peroxymonopersulfate is another optional inorganic perhydrate salt of use in the detergent compositions herein.

The inorganic perhydrate bleaches are preferably present at a level of from 1% to 40% by weight, more preferably from 3% to 35% by weight, most preferably from 5% to 20% by weight of the detergent composition.

Leaving groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:



and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group. Any of R^1 , R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl,

hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

The preferred solubilizing groups are $-\text{SO}_3^-\text{M}^+$, $-\text{CO}_2^-\text{M}^+$, $-\text{SO}_4^-\text{M}^+$, $-\text{N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O}-\text{N}(\text{R}^3)_3$ and most preferably $-\text{SO}_3^-\text{M}^+$ and $-\text{CO}_2^-\text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Preferred hydrophilic and hydrophobic precursors

Suitable bleach precursors typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Alkyl percarboxylic acid bleach precursors

Alkyl percarboxylic acid bleach precursors are preferred precursors for use herein. They form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred can be phenyl esters of C_{14-22} - alkanolic or alkenolic acids, esters of hydroxylamine, geminal diesters of lower alkanolic acids and gem-idols, such as those described in EP-A-0125781 especially 1,1,5-triacetoxypent-4-ene and 1,1,5,5-tetraacetoxypentane and the corresponding butene and butane compounds, ethylidene benzoate acetate and bis(ethylidene acetate) adipate and enol esters, for instance as described in EP-A-0140648 and EP-A-0092932.

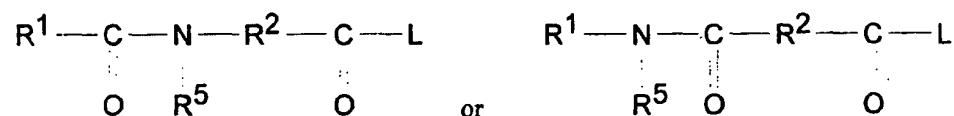
Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group

contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED, being a hydrophilic precursor) is particularly preferred.

Other highly preferred alkyl percarboxylic acid precursors include sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose, dodecanolyloxy - benzenesulphonate sodium salt, decanoyloxy - benzenesulphonate sodium salt (DOBS), benzoyloxy - benzenesulphonate sodium salt (BOBS), more preferred sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS) and even more preferred sodium nonanoyloxybenzene sulfonate (NOBS), (being hydrophobic precursors).

Amide substituted alkyl peroxyacid precursors

Amide substituted alkyl peroxyacid precursors are preferred precursors herein. They include those of the following general formulae:



wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

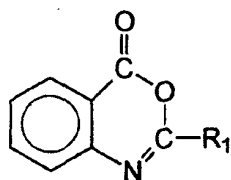
Perbenzoic acid precursor

Perbenzoic acid precursors are other preferred precursors herein. They provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Highly preferred hydrophobic precursors are (6-octanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzene- sulfonate, (6-nonanamidocaproyl)oxy benzene sulfonate, decanoyloxy - benzenesulphonate sodium salt and benzoyloxy - benzenesulphonate sodium salt.

Benzoxazin organic peroxyacid precursors

Also suitable are precursors of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:



wherein R₁ is H, alkyl, alkaryl, aryl, or arylalkyl.

Additional detergent components

The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the washing operation for which it is to be used.

The compositions of the invention preferably contain one or more additional detergent components selected from additional surfactants, additional bleaches, bleach catalysts, alkalinity systems, builders, organic polymeric compounds, additional enzymes, suds suppressors, lime soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

Additional surfactant

The detergent compositions of the invention preferably contain an additional surfactant selected from additional anionic, nonionic, cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Where present, ampholytic, amphoteric and zwitteronic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic surfactant

The detergent compositions of the present invention preferably comprise an additional anionic surfactant. Essentially any anionic surfactants useful for deterative purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12} - C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6 - C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5 - C_{17} acyl-N-(C_1 - C_4 alkyl) and -N-(C_1 - C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C₁₀-C₁₈ alkyl sulfates, more preferably the C₁₁-C₁₅ branched chain alkyl sulfates and the C₁₂-C₁₄ linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₁₀-C₁₈ alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₁₁-C₁₈, most preferably C₁₁-C₁₅ alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula RO(CH₂CH₂O)_xCH₂COO⁻M⁺ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula RO-(CHR₁-CHR₂-O)-R₃ wherein R is a C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R₃ is selected from the group consisting of

hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula $R-CON(R^1)CH_2COOM$, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Alkoxyated nonionic surfactant

Essentially any alkoxyated nonionic surfactants are suitable herein. The ethoxyated and propoxyated nonionic surfactants are preferred.

The nonionic surfactant is preferably present at a ratio to the surfactant system a0, comprising the mid-branched surfactants of the invention, of from 10:1 to 1:10, more preferably from 5:1 to 1:10, even more preferably from 1:1 to 1:10.

Preferred alkoxyated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxyated alcohols, nonionic ethoxyated/propoxyated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic alkoxyated alcohol surfactant

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or

secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms, more preferably from 9 to 15 carbon atoms, with from 3 to 12 moles of ethylene oxide per mole of alcohol.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein: R^1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{31} hydrocarbyl, preferably straight-chain C_5 - C_{19} alkyl or alkenyl, more preferably straight-chain C_9 - C_{17} alkyl or alkenyl, most preferably straight-chain C_{11} - C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxyated or propoxyated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycyl.

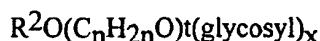
Nonionic fatty acid amide surfactant

Suitable fatty acid amide surfactants include those having the formula: $R^6CON(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10} - C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl-amphocarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula $R(R^1)_2N^+R^2COO^-$ wherein R is a C_6 - C_{18} hydrocarbyl group, each R^1 is typically C_1 - C_3 alkyl, and R^2 is a C_1 - C_5 hydrocarbyl group. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

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Cationic surfactants

Additional cationic surfactants can also be used in the detergent compositions herein. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Alkalinity

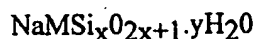
In the detergent compositions of the present invention preferably an alkalinity system is present to achieve optimal cationic ester surfactant performance. The alkalinity system comprises components capable of providing alkalinity species in solution. By alkalinity species it is meant herein: carbonate, bicarbonate, hydroxide, the various silicate anions, percarbonate, perborates, perphosphates, persulfate and persilicate.

Such alkalinity species can be formed for example, when alkaline salts selected from alkali metal or alkaline earth carbonate, bicarbonate, hydroxide or silicate, including crystalline layered silicate, salts and percarbonate, perborates, perphosphates, persulfate and persilicate salts, as described above, and any mixtures thereof, are dissolved in water.

Examples of carbonates are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Suitable silicates include the water soluble sodium silicates with an SiO₂: Na₂O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.0 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO₂: Na₂O ratio of 2.0 is the most preferred silicate.

Preferred crystalline layered silicates for use herein have the general formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. Herein, x in the general formula above preferably has a value of 2, 3 or 4 and is preferably 2. The most preferred material is δ -Na₂Si₂O₅, available from Hoechst AG as NaSKS-6.

Water-soluble builder compound

The detergent compositions of the present invention preferably contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, phosphates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Partially soluble or insoluble builder compound

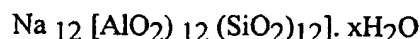
The detergent compositions of the present invention may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates.

Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline,

containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula

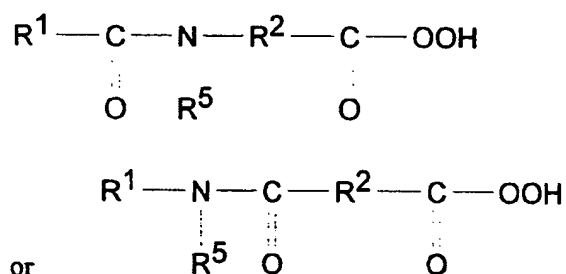


wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86} [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$.

Preformed organic peroxyacid

The detergent compositions or the bleaching system may contain, in addition to the bleach precursors, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:

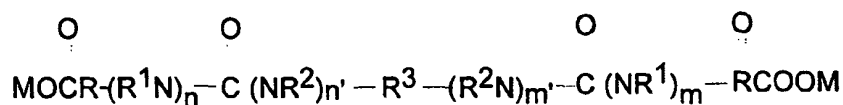


wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Other suitable organic peroxyacids include diperoxyalkanedioic acids having more than 7 carbon atoms, such as diperoxydodecanedioic acid (DPDA), diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid (PAP), nonanoylamido peroxy-adipic acid (NAPAA) decanoyl- or dodecanoylamidoperoxy acids and hexane sulphenoyl peroxypropionic acid and are also suitable herein.

Other suitable organic peroxyacids include diamino peroxyacids, which are disclosed in WO 95/ 03275, with the following general formula:



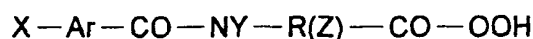
wherein:

R is selected from the group consisting of C₁-C₁₂ alkylene, C₅-C₁₂ cycloalkylene, C₆-C₁₂ arylene and radical combinations thereof;

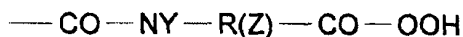
R¹ and R² are independently selected from the group consisting of H, C₁-C₁₆ alkyl and C₆-C₁₂ aryl radicals and a radical that can form a C₃-C₁₂ ring together with R³ and both nitrogens; R³ is selected from the group consisting of C₁-C₁₂ alkylene, C₅-C₁₂ cycloalkylene and C₆-C₁₂ arylene radicals; n and n' each are an integer chosen such that the sum thereof is 1; m and m' each are an integer chosen such that the sum thereof is 1; and

M is selected from the group consisting of H, alkali metal, alkaline earth metal, ammonium, alkanolammonium cations and radicals and combinations thereof.

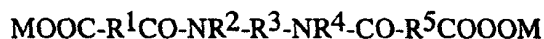
Other suitable organic peroxyacids are include the amido peroxyacids which are disclosed in WO 95/ 16673, with the following general structure:



in which X represents hydrogen or a compatible substituent, Ar is an aryl group, R represents $(CH_2)_n$ in which $n = 2$ or 3 , and Y and Z each represent independently a substituent selected from hydrogen or an alkyl or aryl or alkaryl group or an aryl group substituted by a compatible substituent provided that at least one of Y and Z is not hydrogen if $n = 3$. The substituent X on the benzene nucleus is preferably a hydrogen or a meta or para substituent, selected from the group comprising halogen, typically chlorine atom, or some other non-released non-interfering species such as an alkyl group, conveniently up to C6 for example a methyl, ethyl or propyl group. Alternatively, X can represent a second amido-percarboxylic acid substituent of formula:-



in which R, Y, Z and n are as defined above.



wherein R^1 is selected from the group consisting of C_1 - C_{12} alkylene, C_5 - C_{12} cycloalkylene, C_6 - C_{12} arylene and radical combinations thereof; R

It may be found to be particularly useful to mix the pre-formed peracid and cationic surfactant together prior to incorporation with any other components of the detergent composition.

Cationic peroxyacid precursors

Cationic peroxyacid precursors can be suitable additional components of the detergent compositions or bleaching systems herein. They produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter.

Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

Bleach catalyst

The compositions optionally contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-}$

O)₆(1,4,7-triazacyclononane)₄-(ClO₄)₂, Mn^{III}Mn^{IV}₄(u-O)₁(u-OAc)₂-(1,4,7-trimethyl-1,4,7-triazacyclononane)₂-(ClO₄)₃, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)(OCH₃)₃-(PF₆). Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including N₄Mn^{III}(u-O)₂Mn^{IV}N₄⁺ and [Bipy₂Mn^{III}(u-O)₂Mn^{IV}bipy₂](ClO₄)₃.

Further suitable bleach catalysts are described, for example, in European patent application No. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Heavy metal ion sequestrant

The detergent compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequesterant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequesterant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.

Enzyme

Another preferred ingredient useful in the detergent compositions is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α -amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of *Humicola* sp., *Thermomyces* sp. or *Pseudomonas* sp. including *Pseudomonas pseudoalcaligenes* or *Pseudomas fluorescens*. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention, and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Suds suppressing system

The detergent compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali

metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkylamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises

(a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Clay softening system

The detergent compositions may contain a clay softening system comprising a clay mineral compound and optionally a clay flocculating agent.

The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents No.s 3,862,058, 3,948,790, 3,954,632 and 4,062,647. European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe suitable organic polymeric clay flocculating agents.

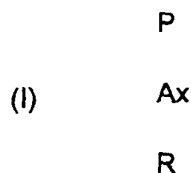
Polymeric dye transfer inhibiting agents

The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof.

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :



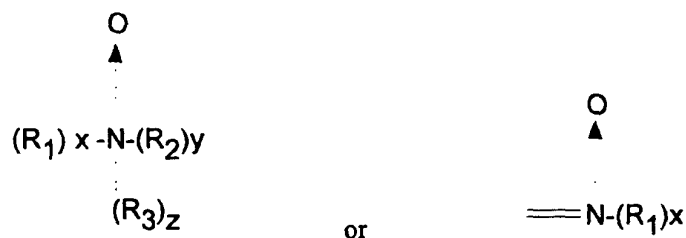
wherein P is a polymerisable unit, and



A is NC, CO, C, -O-, -S-, -N-; x is 0 or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R

is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides where the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic group wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1,000,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Suitable herein are copolymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

d) Polyvinylloxazolidone

The detergent compositions herein may also utilize polyvinylloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinylloxazolidones have an average molecular weight of from 2,500 to 400,000.

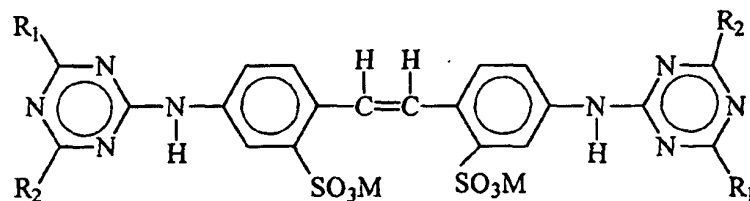
e) Polyvinylimidazole

The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical brightener

The detergent compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include colours and filler salts, with sodium sulfate being a preferred filler salt.

pH of the compositions

The present compositions preferably have a pH measured as a 1% solution in distilled water of at least 8.5, preferably from 9.0 to 12.5, most preferably from 9.5 to 11.0.

Form of the compositions

The compositions in accordance with the invention can take a variety of physical preferably solid forms including granular, tablet, bar forms.

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

The mid-chain branched surfactant system herein, preferably with additional surfactants, is preferably present in granular compositions in the form of surfactant agglomerate particles, preferably not comprising the bleach precursors, which may take the form of flakes, prills, marumes, noodles, ribbons, but preferably take the form of granules. The most preferred way to process the particles is by agglomerating powders (e.g. aluminosilicate, carbonate) with high active surfactant pastes and to control the particle size of the resultant agglomerates within specified limits. Such a process involves mixing an effective amount of powder with a high active surfactant paste in one or more agglomerators such as a pan agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands, and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used, such as a Lodige CB (Trade Name).

A high active surfactant paste comprising from 50% by weight to 95% by weight, preferably 70% by weight to 85% by weight of the surfactants, including the mid-chain branched surfactants, is typically used. The paste may be pumped into the agglomerator at a temperature high enough to maintain a pumpable viscosity, but low enough to avoid degradation of the anionic surfactants used. An operating temperature of the paste of 50°C to 80°C is typical.

The bleach precursors of the invention are preferably dry-added to the detergent base or the agglomerates.

The mean particle size of the components of granular compositions in accordance with the invention should preferably be such that no more than 5% of particles are greater than 1.7mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 300 g/litre, more preferably from 330 g/litre to 1200 g/litre, more preferably from 380g/litre to 850 g/litre. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

The compositions in accord with the present invention can also be used in or in combination with bleach additive compositions, for example comprising chlorine bleach, as mentioned above.

However, since preferred detergent compositions of the invention are solid, most liquid chlorine-based bleaching will not be suitable for these detergent compositions and only granular or powder chlorine-based bleaches will be suitable.

Alternatively, the detergent compositions can be formulated such that they are chlorine-based bleach-compatible, thus ensuring that a chlorine based bleach can be added to the detergent composition by the user at the beginning or during the washing process.

The chlorine-based bleaches such that a hypochlorite species is formed in aqueous solution. The hypochlorite ion is chemically represented by the formula OCI^- .

Those bleaching agents which yield a hypochlorite species in aqueous solution include alkali metal and alkaline earth metal hypochlorites, hypochlorite addition products, chloramines, chlorimines, chloramides, and chlorimides. Specific examples of compounds of this type include sodium hypochlorite, potassium hypochlorite, monobasic calcium hypochlorite, dibasic magnesium hypochlorite, chlorinated trisodium phosphate dodecahydrate, potassium dichloroisocyanurate, sodium dichloroisocyanurate sodium dichloroisocyanurate dihydrate, trichlorocyanuric acid, 1,3-dichloro-5,5-dimethylhydantoin, N-chlorosulfamide, Chloramine T, Dichloramine T, chloramine B and Dichloramine B. A preferred bleaching agent for use in the compositions of the instant invention is sodium hypochlorite, potassium hypochlorite, or a mixture thereof. A preferred chlorine-based bleach can be Triclosan (trade name).

Most of the above-described hypochlorite-yielding bleaching agents are available in solid or concentrated form and are dissolved in water during preparation of the compositions of the instant invention. Some of the above materials are available as aqueous solutions.

Laundry washing method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. The volume capacity should be such as to be able

to contain sufficient detergent product as would normally be used in the washing method.

Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use with the composition of the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in *Manufacturing Chemist*, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly known as the "granulette". Another preferred dispensing device for use with the compositions of this invention is disclosed in PCT Patent Application No. WO94/11562.

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The

support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

Packaging for the compositions

Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in European Application No. 94921505.7.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C ₁₂ alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
C45AS	:	Sodium C ₁₄ -C ₁₅ linear alkyl sulfate
MES	:	-sulpho methylester of C ₁₈ fatty acid
CxyEzS	:	Sodium C _{1x} -C _{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
MBAS _{x,y}	:	Sodium mid-chain branched alkyl sulfate having an average of x carbon atoms, whereof an average of y carbon atoms are comprised in (a) branching unit(s)

C ₄₈ SAS	:	Sodium C ₁₄ -C ₁₈ secondary alcohol sulfate
SADE2S	:	Sodium C ₁₄ -C ₂₂ alkyl disulfate of formula 2-(R).C ₄ H ₇ -1,4-(SO ₄ ⁻) ₂ where R = C ₁₀ OC ₁₈ , condensed with z moles of ethylene oxide
C45E7	:	A C ₁₄₋₁₅ predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
CxyEz	:	A C _{1x-1y} branched primary alcohol condensed with an average of z moles of ethylene oxide
QAS II	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = 50%-60% C ₉ ; 40%-50% C ₁₁
QAS IV	:	R ₁ .N ⁺ (CH ₃)(C ₂ H ₄ OH) ₂ with R ₁ = C ₁₂ -C ₁₄
QAS V	:	R ² O(C ₂ H ₄ O) _x (glycosyl) ₂ , wherein R ² is a C ₈ -C ₁₀ alkyl group ; t is from 2 to 8
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
TPKFA	:	C ₁₂ -C ₁₄ topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate
Zeolite A	:	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (Al ₁₀ Si ₂ O ₂) ₁₂ . 27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers
NaSKS-6	:	Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅
Citric acid	:	Anhydrous citric acid
Carbonate	:	Anhydrous sodium carbonate with a particle size between 200μm and 900μm
Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
Silicate	:	Amorphous Sodium Silicate (SiO ₂ :Na ₂ O; 2.0 ratio)
Sodium sulfate	:	Anhydrous sodium sulfate
Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and q 850μm
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
CMC	:	Sodium carboxymethyl cellulose
Protease	:	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase

Alcalase	:	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
Cellulase	:	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
Amylase	:	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
Lipase	:	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
Endolase	:	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
Percarbonate	:	Sodium Percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
NAC-OBS	:	(Nonanamido caproyl) oxybenzene sulfonate in the form of the sodium salt.
NOBS	:	Nonanoyl oxybenzene sulfonate in the form of the sodium salt
LOBS	:	Dodecanoyl oxybenzene sulfonate in the form of the sodium salt
DOBS	:	Decanoyl oxybenzene sulfonate in the form of the sodium salt
DPDA	:	Diperoxydodecanedioic acid
PAP	:	N-phthaloylamidoperoxicaproic acid
NAPAA	:	Nonanoylamido peroxo-adipic acid
NACA	:	6 nonylamino - 6 oxo - capronic acid.
TAED	:	Tetraacetythylenediamine
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
Photoactivated	:	Sulfonated Zinc or aluminium Phthlocyanine encapsulated
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl

Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
HEDP	:	1,1-hydroxyethane diphosphonic acid
PVNO	:	Polyvinylpyridine N-oxide
PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole
QEA	:	bis $((C_2H_5O)(C_2H_4O)_n)$ $(CH_3)^+-N^+-C_6H_{12}-N^+-(CH_3)$ bis $((C_2H_5O)-(C_2H_4O)_n)$, wherein n=from 20 to 30
SRP 1	:	Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
SRP 2	:	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

In the following Examples all levels are quoted as parts per weight of the composition or % by weight of the composition, as indicated:

Example 1

The following high density granular laundry detergent compositions A to F of particular utility under European machine wash conditions were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	8.0	8.0	-	2.0	8.0	6.0
MES	-	-	5.0	-	-	6.0
TAS	-	0.5	-	0.5	1.00	1.5
C25E3	3.4	-	-	3.4	5.4	2.4
C25E7	-	3.0	4.5	-	-	-
C46AS	2.0	2.0	2.5	-	-	-
C24AS	-	-	-	7.0	4.0	5.0
SADS	-	-	-	-	1.0	-
MBAS 165, 1.8	6.0	-	8.0	10	-	5.0
MBAS16.5, 2.8	-	7.0	-	-	8.0	5.0
QAS II	-	-	0.8	-	-	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Citric acid	2.0	1.0	-	-	-	-
Silicate	1.4	1.4	1.4	3.0	3.0	3.0

Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
PB4	9.0	9.0	9.0	-	-	-
Percarbonate	-	-	-	18.0	15.0	20.0
TAED	0.5	1.0	4.0	1.5	1.0	1.0
NAC-OBS	4.0	2.5	0.5	1.0	2.0	5.0
DTPMP	0.25	0.25	0.25	0.25	0.25	0.25
EDDS	-	-	0.25	0.4	-	-
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
QEA	0.5	1.0	-	-	0.5	-
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.1	0.1	0.1	0.1
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Density in g/litre	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions G to I of bulk density 750 g/litre are compositions according to the invention:

	G	H	I
LAS	12.0	10.0	7.0
TAS	1.25	2.86	1.57
C45AS	3.5	3.24	2.0
C25AE3S	-	0.76	1.0
C45E7	3.25	-	-
C25E3	-	3.5	3.5
QAS I	0.8	2.0	-
MBAS 17, 1.7	7.0	-	5.0
MBAS 17, 2.5	-	2.0	-
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/silicate (79:21)	-	10.6	10.6
Citric acid/citrate	2.0	4.0	1.0
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0

Silicate	6.8	-	-
Sodium sulfate	39.8	-	7.0
PB4	5.0	12.7	-
Percarbonate	-	-	16.0
TAED	0.5	0.7	2.0
NAC OBS	1.0	2.2	2.0
DTPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Protease	0.26	0.85	0.85
Lipase	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28
Amylase	0.1	0.1	0.1
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4
PVP	-	-	0.8
Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm
Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04

Perfume	0.3	0.3	0.3
Silicone antifoam	0.5	2.4	2.4
Minors/misc to 100%	n.a.	n.a.	

Example 3

The following are detergent formulations, according to the present invention where J is a phosphorus-containing detergent composition, K is a zeolite-containing detergent composition and L is a compact detergent composition:

	J	K	L	M
Blown Powder				
STPP	24.0	-	24.0	-
Zeolite A	-	24.0	-	24.0
C45AS	9.0	-	4.0	13.0
QAS I	-	1.0	-	-
MBAS 17, 1.7	4.0	-	10.0	6.0
MBAS 17, 3.5	2.0	11.0	-	-
SADS	2.0	-	-	-
C25AE ₃ S	-	1.0	-	1.0
MA/AA	2.0	4.0	2.0	4.0
LAS	6.0	12.0	13.0	5
TAS	-	1.0	2.0	-
Silicate	7.0	3.0	3.0	3.0
CMC	1.0	1.0	0.5	1.0
Brightener 2	0.2	0.2	0.2	0.2
Soap	1.0	-	-	1.0
DTPMP	0.4	0.4	0.2	0.4
Spray On				
C45E7	-	2.5	-	-
C25E3	2.5	-	-	1.5
Silicone antifoam	0.3	0.3	0.3	0.3
Perfume	0.3	0.3	0.3	0.3
Dry additives				
QEA	-	0.5	1.0	-
Carbonate	6.0	13.0	15.0	13.0
PB4	18.0	18.0	5.0	-
PB1	4.0	-	-	14.0

NOBS	3.0	4.2	-	6.0
TAED	1.0	1.0	5.0	1.0
LOBS	-	-	2.0	-
Photoactivated bleach	0.02	0.02	0.02	0.02
Manganese catalyst	-	-	0.5	-
Protease	1.0	1.0	1.0	1.0
Lipase	0.4	0.4	0.4	0.4
Amylase	0.25	0.30	0.15	0.3
Dry mixed sodium sulfate	3.0	3.0	5.0	3.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0	100.0
Density (g/litre)	630	670	670	670

Example 4

The following are detergent formulations according to the present invention:

	N	O	P	Q
LAS	20.0	14.0	13.0	20.0
TAS	-	1.0	4.0	-
MBAS 16.5, 1.9	2.0	10.0	2.0	8.0
C45AS	4.0	4.0	6.0	6.0
MES	3.0	-	-	-
QAS II	-	0.4	1.0	-
TFAA	-	1.0	-	-
C25E5/C45E7/C25E3	-	2.0	-	1.0
STPP	30.0	18.0	30.0	22.0
Silicate	9.0	5.0	10.0	8.0
Carbonate	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DTPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.15	0.05	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2

PBI	6.0	2.0	-	-
Percarbonate	-	-	12.0	15.0
NACA	-	-	-	3.0
NAC OBS	2.0	-	-	3.1
TAED	2.0	4.0	2.0	1.0
DOBS	-	-	2.0	-
LOBS	-	3.0	-	-
Balance (Moisture and Miscellaneous)	100	100	100	100

Example 5

The following are detergent formulations according to the present invention:

	R	S	T
Blown Powder			
MBAS 16.5,1.7	6.0	10.0	-
MBAS 17.5, 3.0	-	-	12.0
Zeolite A	30.0	22.0	6.0
Sodium sulfate	19.0	5.0	7.0
MA/AA	3.0	3.0	6.0
LAS	3.0	9.0	3.5
C45AS	5.0	4.0	7.0
Silicate	-	1.0	5.0
Soap	-	-	2.0
Brightener 1	0.2	0.2	0.2
Carbonate	8.0	16.0	20.0
Spray On			
C45E5	1.0	1.0	-
Dry additives			
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
TAED	6.4	2.0	2.0
NOBS	-	6.1	-
NAC OBS	-	-	4.5
Percarbonate	-	-	16.0
PBI	-	10.0	-
PB4	8.0	-	-

Sodium sulfate	-	6.0	-
Balance (Moisture and Miscellaneous)	100	100	100

Example 6

The following are high density and bleach-containing detergent formulations according to the present invention:

	U	V	W
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodium sulfate	0.0	5.0	0.0
LAS	3.0	-	3.0
C45AS	3.0	2.0	4.0
QAS	-	-	1.5
DTPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	6.0	4.0	1.0
MBAS 16.5, 1.6	2.0	5.0	10.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Encapsulated Perfume	0.3	0.3	0.3
C25E3	2.0	-	-
Dry additives			
QEA	-	-	0.5
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	1.0	0.5	3.0
NACAOBS	6.0	-	5.0
LOBS/ DOBS	-	1.0	-
Manganese catalyst	-	-	0.3
NOBS	-	2.0	-
PB1	14.0	7.0	10.0
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0

Citric acid	-	-	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 7

The following are high density detergent formulations according to the present invention:

	X	Y
Agglomerate		
MES	-	8.0
LAS	12.0	-
TAS	-	2.0
C45AS	6.0	4.0
MBAS17.5, 1.6	4.0	3.0
MBAS17.5, 2.8	4.0	-
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DTPMP	0.4	0.4
Spray On		
C25E3	1.0	1.0
Perfume	0.5	0.5
Dry Adds		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	-	1.0
Citric acid	2.0	-
NAC OBS	4.1	-
LOBS	-	3.0

TAED	0.8	2.0
Percarbonate	20.0	20.0
SRP 1	0.3	0.3
Protease	1.4	1.4
Lipase	0.4	0.4
Cellulase	0.6	0.6
Amylase	0.6	0.6
QEA	1.0	-
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Density (g/litre)	850	850

Example 8

The following granular detergent formulations are examples of the present invention.

	AH	AI	AJ
Blown powder			
MES	-	6.0	-
LAS	12.0	-	13.0
C45AS	-	4.0	-
C46AS	4.0	-	-
C45AE35	2.0	5.0	3.0
MBAS17, 2.2	5.0	-	2-
Zeolite A	16.0	19.0	16.0
MA/AA	3.0	-	-
AA	3.0	2.0	3.0
Sodium sulfate	3.3	24.0	13.3
Silicate	1.0	2.0	1.0
Carbonate	9.0	25.7	8.0
QEA	0.4	-	0.5
PEG 4000	-	1.0	1.5
Brightener	0.3	0.3	0.3
Spray on			
C25E5	0.5	1.0	-
Perfume	0.3	1.0	0.3
Agglomerates			
C45AS	5.0	2.0	5.0
LAS	1.0	1.0	2.0
MBAS17, 1.6	-	4.0	5.0
Zeolite A	7.5	-	7.5
HEDP	1.0	-	2.0

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Carbonate	4.0	-	4.0
PEG 4000	0.5	-	0.5
Misc (water etc)	2.0	-	2.0
Dry additives			
LOBS/DOBS/NOBS	4.0	4.0	-
TAED	-	-	2.0
NACA-OBS	-	-	3.0
PB4	14.0	-	2.0
PB1	-	7.0	-
Carbonate	5.3	-	2.5
Cumene sulfonic acid	2.0	-	2.0
Lipase	0.4	0.1	0.05
Cellulase	0.2	-	0.2
Amylase	0.3	-	-
Protease	1.6	-	1.6
PVPVI	0.5	-	-
PVNO	0.5	-	-
SRP1	0.5	-	-
Silicone antifoam	0.2	-	0.2

Example 9

	AK	AL	AM	AN	AO	AP
C45AS	11.0	5.1	4.0	8.5	4.1	9.8
C25AES	1.3	1.0	-	1.3	1.0	-
LAS	9.4	6.6	20.5	3.7	1.7	4.0
C25E3/ C25E5	1.5	4.7	3.3	1.5	4.7	3.30
MBAS 16.5, 1.7	10.0	5.0	3.0	12.2	5.9	14.1
QAS	-	1.15	0.4	-	1.7	-
Zeolite A	27.0	16.7	11.2	27.0	16.7	11.2
SKS-6	-	9.0	7.5	-	9.0	7.5
Citric acid	-	1.5	-	-	1.5	-
MA/AA	-	0.6	-	-	0.6	-
MA/AA 3	-	-	7.0	-	-	7.0
AA	2.2	-	-	2.2	-	-
EDDS	-	0.3	-	-	0.3	-
HEDP	-	0.5	-	-	0.5	-
Carbonate	26.0	12.5	14.9	26.5	12.5	14.9
Silicate	0.5	0.8	12	0.5	0.8	12

PB1	11.0	-	3.9	7.0	-	3.9
NOBS	3.0	2.7	4.0	-	-	4.0
NACA-OBS	-	2.7	-	4.0	2.75	-
PC	-	17.3	-	-	17.3	-
TAED	5.0	3.5	2.0	1.0	3.5	4.0
Protease	0.26	0.3	0.2	0.2	0.3	0.2
Lipase	-	-	-	-	-	-
Carezyme IT	0.33	0.26	-	0.33	0.26	-
Termamyl 120T	-	0.36	-	-	0.36	-
Brightener	0.17	0.06	0.30	0.17	0.06	0.30
SRP1	0.4	0.2	0.5	0.4	0.2	0.5
PEG	1.6	-	0.19	1.6	-	0.19
Sulfate	5.3	6.4	3.4	5.3	6.4	3.4
CMC	-	0.5	-	-	0.5	-
MgSO ₄	-	0.13	-	-	0.13	-
Photobleach	-	0.0026	-	-	0.0026	-
Silicone anti-foam	-	0.21	0.17	0.02	0.21	0.17
Perfume	0.42	0.55	0.25	0.42	0.55	0.25

Example 10

The following laundry detergent compositions AQ to AT are prepared in accord with the invention:

	AQ	AR	AS	AT
MBAS 16.5, 1.8	22	16.5	11	5.5
C45 AS	8	10	11	4
C45E1S	4	3	-	1
LAS	8	14	-	4
C16 SAS	-	-	3	-
MES	-	-	12	-
C23E6.5	1.5	1.5	1.5	1.5
Zeolite A	17.8	20.8	20.8	27.8
AA	2.3	2.3	2.3	2.3
Carbonate	27.3	27.3	27.3	27.3
Silicate	0.6	0.6	0.6	0.6
Perborate	1.0	1.0	1.0	1.0
Protease	0.3	0.3	0.3	0.3
Cellulase	0.3	0.3	0.3	0.3
SRP1	0.4	0.4	0.4	0.4

Brightener	0.2	0.2	0.2	0.2
PEG	1.6	1.6	1.6	1.6
PBI	16.0	6.0		
NOBS	2.4	4.5	0.8	3.5
PC			8.0	15.0
Sulfate	5.5	5.5	5.5	5.5
Silicone Antifoam	0.42	0.42	0.42	0.42
TAED	0.5	4.5	8.0	2.0
Moisture & Minors	---Balance---			
Density (g/L)	660	660	660	660

Example 11

The following laundry detergent compositions AU to AY are prepared in accord with the invention:

	AU	AV	AW	AX	AY
MBAS 16.5, 1.7	14.8	16.4	12.3	8.2	4.1
C45 AS	5	7	6	4	12
C45E3S	2	-	4	-	5
LAS	14	8	-	18	5
C16 SAS	-	-	1	-	1
MES	-	-	10	-	-
TFAA	1.6	0	0	0	0
C24E3	4.9	4.9	4.9	4.9	4.9
Zeolite A	15	15	15	15	15
QAS	1.0	1.5	-	-	1.0
NaSKS-6	11	11	11	11	11
Citrate/citric	1.0	2.0	3	3	-
MA/AA	4.8	4.8	4.8	4.8	4.8
HEDP	0.5	0.5	0.5	0.5	0.5
Carbonate	8.5	8.5	8.5	8.5	8.5
Protease	0.9	0.9	0.9	0.9	0.9
Lipase	0.15	0.15	0.15	0.15	0.15
Cellulase	0.26	0.26	0.26	0.26	0.26
Amylase	0.36	0.36	0.36	0.36	0.36
NOBS	-	-	-	4.0	5.0
NACA-OBS	4.0	2.0	6.0	-	-
TAED	4.0	5.0	2.0	1.0	0.5
PBI	-	-	14.0	-	8.0
Percarbonate	20.0	14.0	-	22.0	-
SRP1	0.2	0.2	0.2	0.2	0.2
QEA1	1.0	1.5	-	-	-

Brightener	0.2	0.2	0.2	0.2	0.2
Sulfate	2.3	2.3	2.3	2.3	2.3
Silicone Antifoam	0.4	0.4	0.4	0.4	0.4
Moisture & Minors	---Balance---				
Density (g/L)	850	850		850	850

Example 12

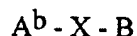
The following laundry detergent compositions AZ to Ee are prepared in accord with the invention:

	AZ	Aa	Bb	Cc	Dd	Ee
MBAS 16.5, 1.7	32	32	24	16	16	8
C45 AS	5	-	6	12	2	-
C45E1S	1	-	-	1	5	2
LAS	-	20	8	23	12	16
C16 SAS	1	4	-	-	-	-
MES	14	-	-	-	-	-
C23E6.5	3.6	3.6	3.6	3.6	3.6	3.6
QAS	-	0.5	-	-	0.5	-
Zeolite A	9.0	9.0	9.0	9.0	9.0	9.0
Polycarboxylate	7.0	7.0	7.0	7.0	7.0	7.0
Carbonate	18.4	18.4	18.4	18.4	18.4	18.4
Silicate	11.3	11.3	11.3	11.3	11.3	11.3
PB1	-	-	3.9	10.0	3.9	15.0
TAED	2.0	5.0	1.0	0.5	6.0	2.0
Percarbonate	7.0	7.0	-	-	-	-
NOBS	4.1	4.1	4.1	4.1	4.1	4.1
Protease	0.9	0.9	0.9	0.9	0.9	0.9
SRP1	0.5	0.5	0.5	0.5	0.5	0.5
Brightener	0.3	0.3	0.3	0.3	0.3	0.3
PEG	0.2	0.2	0.2	0.2	0.2	0.2
Sulfate	5.1	5.1	5.1	5.1	5.1	5.1
Silicone Antifoam	0.2	0.2	0.2	0.2	0.2	0.2
Moisture & Minors	---Balance---					
Density (g/L)	810	810	810	810	810	810

What is claimed is:

1. A detergent composition comprising

a) at least 0.5%, preferably at least 5%, more preferably at least 10% by weight of the composition a surfactant system, comprising one or more longer alkyl chain, mid-chain branched surfactant compounds of the formula:



wherein:

(I) A^b is a hydrophobic mid-chain branched alkyl moiety, having in total 9 to 22 carbons in the moiety, preferably from 12 to about 18, having: (1) a longest linear carbon chain attached to the - X - B moiety in the range of from 8 to 21 carbon atoms; (2) one or more $C_1 - C_3$ alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of the position 2 carbon, counting from position 1 carbon (#1) which is attached to the - X - B moiety, to the position of the terminal carbon minus 2 carbons, (the $(\omega - 2)$ carbon); and (4) when more than one of these compounds is present, the average total number of carbon atoms in the A^b -X moieties in the above formula is within the range of greater than 14.5 to about 18, preferably from about 15 to about 17;

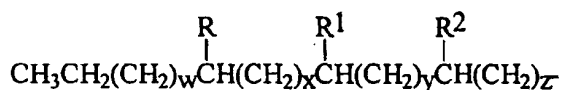
(II) B is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, preferably polyoxyethylene and polyoxypropylene, alkoxyated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polygluconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccinates, polyalkoxyated carboxylates, glucamides, taurinates, sarcosinates, glycinate, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxyated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkylated/polyhydroxyalkylated quats, alkylated quats, alkylated/polyhydroxyalkylated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and

(III) X is selected from $-CH_2-$ and $-C(O)-$; and

b) at least 0.5% by weight of the composition a bleaching system comprising
(I) a hydrophobic bleach precursor; and

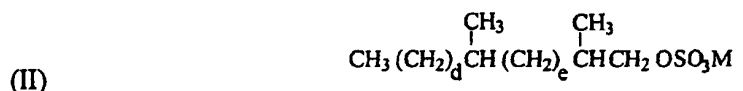
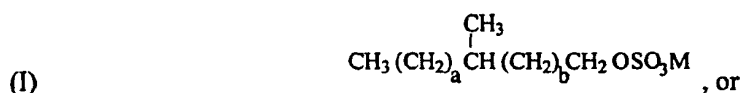
(II) a hydrophilic bleach precursor.

2. A detergent composition according to claim 1 wherein the surfactant compounds of surfactant system a) are of the above formula wherein the A^b moiety is a branched primary alkyl moiety having the formula:



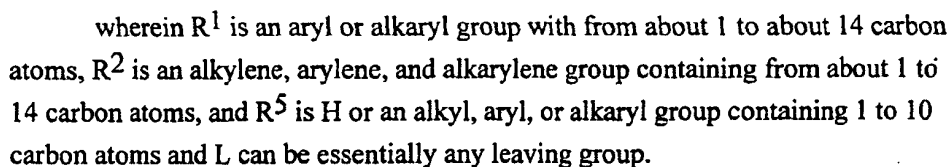
wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula, including the R, R¹, and R² branching, is from 13 to 19; R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl, preferably methyl, provided R, R¹, and R² are not all hydrogen and, when z is 0, at least R or R¹ is not hydrogen; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer from 0 to 13; and w + x + y + z is from 7 to 13.

3. A detergent composition according to any preceding claim wherein the surfactant system a) comprises at least about 20% by weight of the system, more preferably at least 90% by weight, of one or more mid-chain branched alkyl sulfates having the formula:



or mixtures thereof; wherein M represents one or more cations; a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further
when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8;
when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9;
when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10;
when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11;
when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12;
when a + b = 15, a is an integer from 2 to 14 and b is an integer from 1 to 13;

4. A detergent composition according to any preceding claim wherein the surfactant compounds of the surfactant system a) have a $A^b - X$ moiety comprising from 16 to 18 carbon atoms and B is a sulfate group.
5. A detergent composition wherein the hydrophobic bleach precursor is of the formula:



6. A detergent composition according to any preceding claim wherein the hydrophobic bleach precursor is selected from the group comprising (6-octanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzene- sulfonate, (6-nonanamidocaproyl)oxy benzene sulfonate, decanoyloxy - benzenesulphonate sodium salt, benzoyloxy - benzenesulphonate sodium salt, sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate and sodium nonanoyl, decanoyl or dodecanoyloxybenzene sulfonate.

7. A detergent composition according to any preceding claim wherein the hydrophilic bleach precursor is TAED.
8. A detergent composition according to any preceding claim wherein the bleaching system comprises an inorganic perhydrate salt, preferably a perborate or percarbonate salt, preferably at a level of from 3% to 25% by weight of the composition.
9. A detergent composition according to any preceding claim wherein a nonionic surfactant, preferably a C₉₋₁₅ primary alcohol ethoxylate containing from 3-12 moles of ethylene oxide per mole of alcohol, is present at a ratio to the surfactant system a) of from 10:1 to 1:10, preferably 1:1 to 1:10.
10. A detergent composition according to any preceding claim in the form of a solid laundry detergent composition.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/18842

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D1/00 C11D1/14 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 97 39088 A (CONNOR DANIEL STEDMAN ; VINSON PHILLIP KYLE (US); WILLMAN KENNETH W) 23 October 1997 see page 32, line 27 - line 29; examples 9,10 ---	1-9
A	DATABASE WPI Section Ch, Week 8238 Derwent Publications Ltd., London, GB; Class A97, AN 82-80582E XP002066464 & JP 57 133 200 A (KAO SOAP CO LTD) see abstract ---	1
A	EP 0 130 609 A (KAO CORP) 9 January 1985 see claims 1,4,5; examples 2,4; tables 2-1,,2-2 --- -/-	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search

29 May 1998

Date of mailing of the international search report

16/06/1998

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/18842

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

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International Application No

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